第八章 近似方法

1. 定态微扰论（不含时） 求 $\hat{H}$ 的本征态

$\hat{H} = \hat{H}_0 + \hat{V}$ 　要求划分：① $\hat{H}_0$ 简单可解 （或前一级算过） 　$\hat{H}_0 |\psi_n^{(0)}\rangle = E_n^{(0)} |\psi_n^{(0)}\rangle$

② $\langle \hat{V} \rangle \ll \langle \hat{H}_0 \rangle$ 　修正

思路：$|\psi_n^{(0)}\rangle \xrightarrow{\hat{V}} |\psi_n\rangle = \sum_l C_l |\psi_l^{(0)}\rangle$

$E_n^{(0)} \xrightarrow{\hat{V}} E_n$

a. 非简并微扰论

$\hat{H} = \hat{H}_0 + \lambda \hat{V}$ 　$\lambda \ll 1$

$\Rightarrow E_k = E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \cdots$ 　ps: λ 仅作为标记.

$|\psi_k\rangle = |\psi_k^{(0)}\rangle + \lambda |\psi_k^{(1)}\rangle + \lambda^2 |\psi_k^{(2)}\rangle + \cdots$

由 $\hat{H}|\psi_k\rangle = E_k|\psi_k\rangle$

λ 的 0 次近：$\hat{H}_0 |\psi_k^{(0)}\rangle = E_k^{(0)} |\psi_k^{(0)}\rangle$

λ 的 1 次近：$\hat{H}_0 |\psi_k^{(1)}\rangle + \hat{V} |\psi_k^{(0)}\rangle = E_k^{(1)} |\psi_k^{(0)}\rangle + E_k^{(0)} |\psi_k^{(1)}\rangle$

λ 的 2 次近：$\hat{H}_0 |\psi_k^{(2)}\rangle + \hat{V} |\psi_k^{(1)}\rangle = E_k^{(2)} |\psi_k^{(0)}\rangle + E_k^{(1)} |\psi_k^{(1)}\rangle + E_k^{(0)} |\psi_k^{(2)}\rangle$

取 λ 的 1 次近，左边作用 $\langle \psi_m^{(0)}|$，设 $|\psi_k^{(1)}\rangle = \sum_n C_{kn}^{(1)} |\psi_n^{(0)}\rangle$ 　（ps: $C_n^{(1)}$ 默认是 $C_{nk}^{(1)}$）

$\Rightarrow E_m^{(0)} C_{km}^{(1)} + V_{mk} = E_k^{(0)} C_{km}^{(1)} + E_k^{(1)} \delta_{mk}$

$V_{mk} = \langle \psi_m^{(0)} | \hat{V} | \psi_k^{(0)} \rangle$

$m=k$ 时：$E_k^{(1)} = V_{kk}$

$m \neq k$ 时：$C_{km}^{(1)} = \dfrac{V_{mk}}{E_k^{(0)} - E_m^{(0)}}$ ← 这个地方容易反 　　$\langle \psi_n^{(1)} | \psi_n^{(0)} \rangle \equiv 0$

$$\Rightarrow \begin{cases} E_k \approx E_k^{(0)} + V_{kk} & \text{能量的一级近似} \\ |\psi_k\rangle \approx |\psi_k^{(0)}\rangle + \underbrace{\sum_{m\neq k} \dfrac{V_{mk}}{E_k^{(0)} - E_m^{(0)}} |\psi_m^{(0)}\rangle}_{|\psi_k^{(1)}\rangle} & \text{态的一级近似} \end{cases}$$

（实际运用 0 级就行） 　（注意 $m \neq k$，即一级修正这是 $|\psi_k^{(0)}\rangle$ 垂直方向的态）

* λ 的 2 级近似 　$(2 = 1+1)$

$\hat{H}_0 |\psi_k^{(2)}\rangle + \hat{V} |\psi_k^{(1)}\rangle = E_k^{(0)} |\psi_k^{(2)}\rangle + E_k^{(1)} |\psi_k^{(1)}\rangle + E_k^{(2)} |\psi_k^{(0)}\rangle$

设 $|\psi_k^{(2)}\rangle = \sum_n C_{kn}^{(2)} |\psi_n^{(0)}\rangle$

$\Rightarrow \hat{H}_0 \sum_n C_{kn}^{(2)} |\psi_n^{(0)}\rangle + \hat{V} \sum_{n\neq k} \dfrac{V_{nk}}{E_k^{(0)} - E_n^{(0)}} |\psi_n^{(0)}\rangle = E_k^{(0)} \sum_n C_{kn}^{(2)} |\psi_n^{(0)}\rangle + V_{kk} \sum_{n\neq k} \dfrac{V_{nk}}{E_k^{(0)} - E_n^{(0)}} |\psi_n^{(0)}\rangle + E_k^{(2)} |\psi_k^{(0)}\rangle$

左乘 $\langle \psi_m^{(0)}|$：

$\Rightarrow E_m^{(0)} C_{km}^{(2)} + \sum_{n\neq k} \dfrac{V_{mn} V_{nk}}{E_k^{(0)} - E_n^{(0)}} = E_k^{(0)} C_{km}^{(2)} + \dfrac{V_{kk} V_{mk}}{E_k^{(0)} - E_m^{(0)}} (1 - \delta_{mk}) + E_k^{(2)} \delta_{mk}$

$m=k$ 时：$E_k^{(2)} = \sum_{n\neq k} \dfrac{|V_{nk}|^2}{E_k^{(0)} - E_n^{(0)}}$

$m\neq k$时： $C_m^{(2)} = \dfrac{1}{E_k^{(0)}-E_m^{(0)}}\left(\sum\limits_{n\neq k}\dfrac{V_{mn}V_{nk}}{E_k^{(0)}-E_n^{(0)}} - \dfrac{V_{kk}V_{mk}}{E_k^{(0)}-E_m^{(0)}}\right)$

$$\Rightarrow \begin{cases} E_k \simeq E_k^{(0)} + V_{kk} + \sum\limits_{n\neq k}\dfrac{|V_{nk}|^2}{E_k^{(0)}-E_n^{(0)}} \\ |\psi_k\rangle \simeq |\psi_k^{(0)}\rangle + \sum\limits_{m\neq k}\dfrac{V_{mk}}{E_k^{(0)}-E_m^{(0)}}|\psi_m^{(0)}\rangle \end{cases}$$

(一阶微扰是对角元，二阶微扰是耦合项参与)

$$|\psi_k\rangle = |\psi_k^{(0)}\rangle + \sum_{n\neq k}\frac{V_{nk}}{E_k^{(0)}-E_n^{(0)}}|\psi_n^{(0)}\rangle + \sum_{m\neq k}\frac{1}{E_k^{(0)}-E_m^{(0)}}\left(\sum_{n\neq k}\frac{V_{mn}V_{nk}}{E_k^{(0)}-E_n^{(0)}} - \frac{V_{kk}V_{mk}}{E_k^{(0)}-E_m^{(0)}}\right)|\psi_m^{(0)}\rangle$$

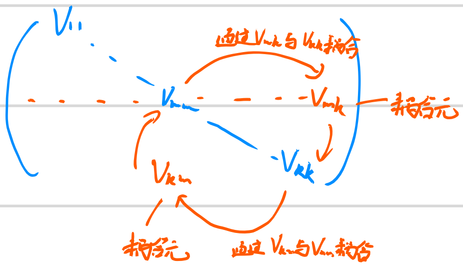
讨论：

i) 正交归一完备性（仅1级近似）

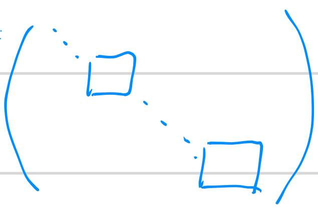
$$\langle\psi_m|\psi_l\rangle = \delta_{ml} + \sum_{n\neq l,k}\frac{V_{ln}V_{nk}}{(E_k^{(0)}-E_n^{(0)})(E_l^{(0)}+E_n^{(0)})}$$

$$\Rightarrow \sum_n|\psi_n\rangle\langle\psi_n| = \hat{I} + O(\lambda^2)$$

ii) 图像理解　　$\hat{V}$在$\{|\psi_n^{(0)}\rangle\}$下表示



iii) 简并？　E_k:



态在非简并元上，可以正常代公式

若在非简并元上，则要用到后面的方法

例： $\hat{H} = \dfrac{\hat{P}^2}{2m} + \dfrac{1}{2}m\omega^2\hat{X}^2 + \dfrac{1}{2}m\omega^2\hat{X}^2\varepsilon$

求能量本征值，精确到ε二阶小量

$E_n^{(0)} = (n+\frac{1}{2})\hbar\omega \qquad |\psi_n^{(0)}\rangle = |n\rangle$

$E_n \approx E_n^{(0)} + \langle n|\hat{V}|n\rangle + \sum\limits_{k\neq n}\dfrac{|V_{nk}|^2}{E_n^{(0)}-E_k^{(0)}}$

由 $\langle m|\hat{X}^2|n\rangle = \dfrac{\hbar}{2m\omega}\left(\sqrt{n(n-1)}\,\delta_{m,n-2} + \sqrt{(n+1)(n+2)}\,\delta_{m,n+2} + (n+1)\delta_{mn} + n\,\delta_{mn}\right)$

$\Rightarrow V_{nn} = \frac{1}{4}(2n+1)\hbar\omega\varepsilon$

?

$V_{kn} = \frac{1}{4}\hbar\omega\varepsilon\left(\sqrt{n(n-1)}\,\delta_{k,n-2} + \sqrt{(n+1)(n+2)}\,\delta_{k,n+2}\right)$

$$\Rightarrow \begin{cases} E_n \simeq (n+\frac{1}{2})\hbar\omega + \frac{1}{4}(2n+1)\hbar\omega\varepsilon - \frac{1}{32}\hbar\omega\varepsilon^2(n+2)(n+1) + \underbrace{\frac{1}{32}\hbar\omega\varepsilon^2 n(n-1)}_{n\geq 2} \\ |\psi_n\rangle \simeq |n\rangle + \frac{1}{8}\varepsilon\left(\underbrace{\sqrt{n(n-1)}\,|n-2\rangle}_{n\geq 2} - \sqrt{(n+1)(n+2)}\,|n+2\rangle\right) \end{cases}$$

特殊情况： $E_0 = \frac{1}{2}\hbar\omega + \frac{1}{4}\hbar\omega\varepsilon - \frac{1}{16}\hbar\omega\varepsilon^2$

$|\psi_0\rangle = |0\rangle - \frac{\sqrt{2}}{8}\varepsilon|2\rangle$

精确解： $E_n = (n+\frac{1}{2})\sqrt{1+\varepsilon}\,\hbar\omega = (n+\frac{1}{2})\hbar\omega\left(1+\frac{\varepsilon}{2}-\frac{\varepsilon^2}{8}+\cdots\right)$

b. 简并微扰论

$\hat{H}_0$的本征态设为 $\{|\psi_{m\mu}^{(0)}\rangle, |\psi_n^{(0)}\rangle\}$　　($m\neq n$，$m\mu$构成一个g维简并子空间)

$$\begin{cases} \hat{H}_0|\psi_{m\mu}^{(0)}\rangle = E_m^{(0)}|\psi_{m\mu}^{(0)}\rangle \\ \hat{H}_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle \end{cases}$$

设 $\begin{cases}|\psi_n\rangle = |\psi^{(0)}\rangle + |\psi^{(1)}\rangle \\ E_n = E_n^{(0)} + E_n^{(1)}\end{cases}$

且设 $\begin{cases}|\psi_n^{(1)}\rangle\text{与简并子空间正交} \\ |\psi_n^{(0)}\rangle\text{可只用简并子空间基}|\psi_{n\nu}^{(0)}\rangle\text{展开}\end{cases}$ $\Rightarrow \begin{cases}|\psi_n^{(0)}\rangle = \sum_\mu C_{n\mu}^{(0)}|\psi_{n\mu}^{(0)}\rangle \\ |\psi_n^{(1)}\rangle = \sum_{m\neq n} C_m^{(1)}|\psi_m^{(0)}\rangle\end{cases}$

λ的一次论表达式

$$\hat{H}_0|\psi_n^{(1)}\rangle + \hat{V}\sum_\mu C_{n\mu}^{(0)}|\psi_{n\mu}^{(0)}\rangle = E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}\sum_\mu C_{n\mu}^{(0)}|\psi_{n\mu}^{(0)}\rangle$$

左乘 $\langle\psi_{n\nu}^{(0)}|$:

$$\sum_\mu V_{n\nu,n\mu} C_{n\mu}^{(0)} = E_n^{(1)} C_{n\nu}^{(0)} \Rightarrow \sum_\mu (V_{n\nu,n\mu} - E_n^{(1)}\delta_{\mu,\nu}) C_{n\mu}^{(0)} = 0$$

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($E_n^{(1)}$与0级波函数绑定得到)

$$\begin{pmatrix} V \end{pmatrix}\begin{pmatrix} C_{n\mu}^{(0)} \end{pmatrix} = E_n^{(1)}\begin{pmatrix} C_{n\mu}^{(0)} \end{pmatrix}$$

即在 $\{|\psi_{n\mu}^{(0)}\rangle\}$ 下，在 $\hat{H}_0$ 的简并子空间里对角化 $\hat{V}$ $\begin{cases}\text{本征值：能量的一级微扰} \\ \text{本征态：简并子空间内新的0级波函数}\end{cases}$

(有点像力学量完备集那一套，$[\hat{H}_0,\hat{V}]=0$)

如简并已消除，则可以继续利用非简并微扰论求高阶修正 ($\psi^{(0)}$已经得到)

否则，需要选择新的0级波函数 (无论如何，根本原则是简并空间中的态不可以有耦合项，如果有必须对角化)

例：$\hat{H}$: $\begin{pmatrix} E_1 & \varepsilon_1 & \varepsilon_2 \\ \varepsilon_1 & E_1 & \\ \varepsilon_2 & & E_2 \end{pmatrix}$ $\varepsilon_1,\varepsilon_2 \ll E_1, E_2$

$\{|\alpha\rangle, |\beta\rangle, |\gamma\rangle\}$

简并子空间 $\begin{pmatrix} & \varepsilon_1 \\ \varepsilon_1 & \end{pmatrix}$ $\Rightarrow \begin{cases}\pm\varepsilon_1 \\ \frac{\sqrt{2}}{2}(|\alpha\rangle \pm |\beta\rangle) \hat{=} |\pm\rangle\end{cases}$

$\Rightarrow$ 1级能量修正 $E_1 \pm \varepsilon_1$

新的零级波函数 $\{|\pm\rangle, |\gamma\rangle\}$

$\Rightarrow \langle +|V|\gamma\rangle = \frac{\sqrt{2}}{2}\varepsilon_2 \quad \langle -|V|\gamma\rangle = \frac{\sqrt{2}}{2}\varepsilon_2$ 新矩阵表示：$\begin{pmatrix} E_1+\varepsilon_1 & & \frac{\sqrt{2}}{2}\varepsilon_2 \\ & E_1-\varepsilon_1 & \frac{\sqrt{2}}{2}\varepsilon_2 \\ \frac{\sqrt{2}}{2}\varepsilon_2 & \frac{\sqrt{2}}{2}\varepsilon_2 & E_2 \end{pmatrix}$

$\Rightarrow$ 2阶: $E_1+\varepsilon_1+\dfrac{\frac{1}{2}\varepsilon_2^2}{E_1-\varepsilon_1-E_2}$ (本来就是 $\dfrac{\frac{1}{2}\varepsilon_2^2}{E_1-E_2}$) ~

$E_1-\varepsilon_1+\dfrac{\frac{1}{2}\varepsilon_2^2}{E_1-\varepsilon_1-E_2}$ 结果和非简并一样

$E_2+\dfrac{\frac{1}{2}\varepsilon_2^2}{E_2-(E_1+\varepsilon_1)}+\dfrac{\frac{1}{2}\varepsilon_2^2}{E_2-(E_1-\varepsilon_1)} = E_2+\dfrac{E_2^2}{E_2-E_1}$

* 能级图像 $\begin{pmatrix} a & c \\ c & b \end{pmatrix}$: 能级排斥

$\begin{pmatrix} a & c \\ c & a \end{pmatrix}$: 简并消除

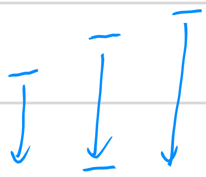
PS: 若 $E_1 \approx E_2$，则是近简并情况，需要对整个 $\hat{V}$ 尝试对角化

* "实际"方法

寻找算符 $\hat{A}$，使 $[\hat{H}_0,\hat{A}]=0$，$[\hat{V},\hat{A}]=0$，且 $\{\hat{H}_0,\hat{A}\}$ 的共同本征态在 $\hat{H}_0$ 的简并子空间中无简并，则这些本征态为好的零级波函数

例: 反常 Zeeman 效应　　(^{23}Na)

3p — — —　$l=1$　　加上 B_z　期望谱线:



3s —　$l=0$

包计入自旋-轨道耦合:　— — — —　$J=\frac{3}{2}$

— —　$J=\frac{1}{2}$　　　不为3条

— —　$J=\frac{1}{2}$

$\hat{H}=A\hat{\vec{L}}\cdot\hat{\vec{S}}+B(\hat{L}_z+2\hat{S}_z)$　(假设已处理 Hamiltonian 其它的部分).

① $A\gg B$　　$\hat{H}_0=A\hat{\vec{L}}\cdot\hat{\vec{S}}=\frac{\hat{\vec{J}}^2-\hat{\vec{S}}^2-\hat{\vec{L}}^2}{2}$　　$\hat{V}=B(\hat{L}_z+2\hat{S}_z)$

选取基为 $\{\hat{J}^2,\hat{J}_z\}\to|j,m_j\rangle$

H_0 矩阵:

$j=l-\frac{1}{2}$，$2l$ 维；$j=l+\frac{1}{2}$，$2l+2$ 维

$$\begin{pmatrix} \begin{pmatrix} -\frac{A}{2}(l+1)\hbar^2 & & \\ & \ddots & \\ & & -\frac{A}{2}(l+1)\hbar^2 \end{pmatrix} & \\ & \begin{pmatrix} \frac{A}{2}l\hbar^2 & & \\ & \ddots & \\ & & \frac{A}{2}l\hbar^2 \end{pmatrix} \end{pmatrix}$$

i) $E_0=\langle j,m_j|\hat{H}_0|j,m_j\rangle=\frac{A}{2}[j(j+1)-l(l+1)-s(s+1)]\hbar^2$

$\Rightarrow\begin{cases} s=\frac{1}{2}\quad j=l+\frac{1}{2}\quad E_0=\frac{A}{2}l\hbar^2 \\ s=\frac{1}{2}\quad j=l-\frac{1}{2}\quad E_0=-\frac{A}{2}(l+1)\hbar^2 \end{cases}$

ii) $\langle j',m_j'|\hat{V}|j,m_j\rangle=B\langle j',m_j'|\hat{J}_z|j,m_j\rangle+B\langle j',m_j'|\hat{S}_z|j,m_j\rangle$

$=Bm_j\hbar\,\delta_{jj'}\delta_{m_j'm_j}+B\langle j',m_j'|\hat{S}_z|j,m_j\rangle$

$\Rightarrow\begin{cases} j=l+\frac{1}{2}:\quad \langle j,m_j'|\hat{S}_z|j,m_j\rangle=\frac{1}{2}\hbar\left(\frac{j+m_j}{2j}-\frac{j-m_j}{2j}\right)\delta_{m_j,m_j'}=\frac{m_j}{2j}\hbar\,\delta_{m_j,m_j'} \text{ (只有对角元)} \\ j=l-\frac{1}{2}:\quad \langle j,m_j'|\hat{S}_z|j,m_j\rangle=-\frac{m_j}{2(j+1)}\hbar\,\delta_{m_j,m_j'} \end{cases}$

$\langle j,m_j'|\hat{S}_z(|m_j+\frac{1}{2},-\frac{1}{2}\rangle C_{-\frac{1}{2}}+|m_j-\frac{1}{2},\frac{1}{2}\rangle C_{\frac{1}{2}})|j,m_j\rangle=-\frac{\hbar}{2}C_{-\frac{1}{2}}^2+\frac{\hbar}{2}C_{\frac{1}{2}}^2$

$=-\frac{\hbar}{2}\frac{j+m_j+1}{2(j+1)}+\frac{\hbar}{2}\frac{j-m_j+1}{2(j+1)}$

iii) 非对角元

$\langle j',m_j'|\hat{J}_z|j,m_j\rangle=0$　(正交).

$\langle j',m_j'|\hat{S}_z|j,m_j\rangle\xrightarrow[j=l+\frac{1}{2}]{j'=l-\frac{1}{2}}\left(-\frac{\hbar}{2}\sqrt{\frac{j+m_j+1}{2j+2}}\sqrt{\frac{j-m_j}{2j}}-\frac{\hbar}{2}\sqrt{\frac{j-m_j+1}{2j+2}}\sqrt{\frac{j+m_j}{2j}}\right)\delta_{m_j'm_j}$

$1+\frac{J(J+1)-L(L+1)+S(S+1)}{2J(J+1)}$

$\Rightarrow$ 简并微扰 (一级)　　Lande 因子.

$j=l+\frac{1}{2}$:　$E_0+E_1=\frac{A}{2}l\hbar^2+B\boxed{\left(m_j+\frac{m_j}{2j}\right)}\hbar$

$j=l-\frac{1}{2}$:　$E_0+E_1=-\frac{A}{2}(l+1)\hbar^2+B\boxed{\left(m_j-\frac{m_j}{2(j+1)}\right)}\hbar$

PS: $[\hat{H}_0,\hat{J}_z]=0$　$[\hat{V},\hat{J}_z]=0$　$\to\{\hat{J}^2,\hat{J}_z\}$ 好!

$[\hat{H}_0,\hat{J}^2]=0$　$[\hat{V},\hat{J}^2]\neq0$

(但忽略二阶).

$1+\frac{j(j+1)-s(s+1)-l(l+1)}{s(s+1)}$.

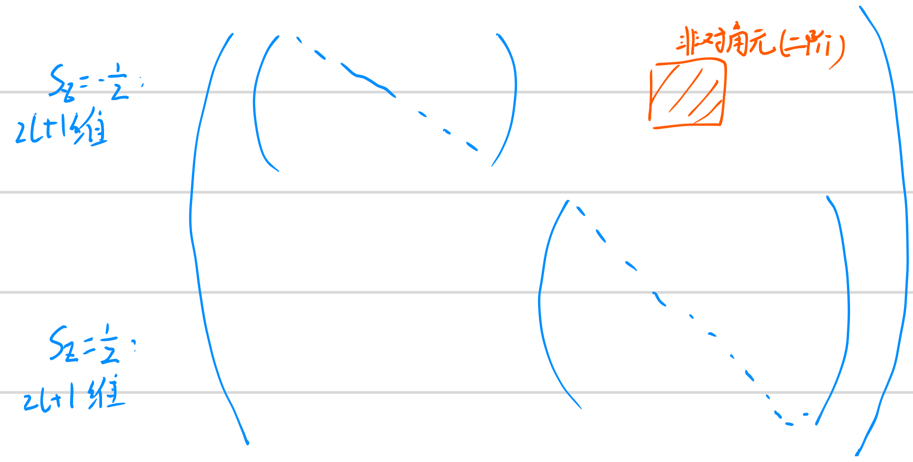
② $A\ll B$

$\hat{H}_0=B(\hat{L}_z+2\hat{S}_z)$　零级: $\{|m_L,S_z\rangle\}$　　$E_0=(m_L+2m_S)B\hbar$

$\hat{V}=A\hat{\vec{L}}\cdot\hat{\vec{S}}$

$\langle m_L'S_z'|\hat{V}|m_LS_z\rangle=A\langle m_L'S_z'|[\hat{L}_z\hat{S}_z+\frac{1}{2}(\hat{L}_+\hat{S}_-+\hat{L}_-\hat{S}_+)]|m_LS_z\rangle$.

$=A\left(m_LS_z\hbar^2\delta_{m_L,m_L'}\delta_{S_z,S_z'}+\ \delta_{S_z',S_z-1}\delta_{m_L',m_L+1}+\ \delta_{S_z',S_z+1}\delta_{m_L',m_L-1}\right)$　(非对角元: $m_L+S_z=m_L'+S_z'$)

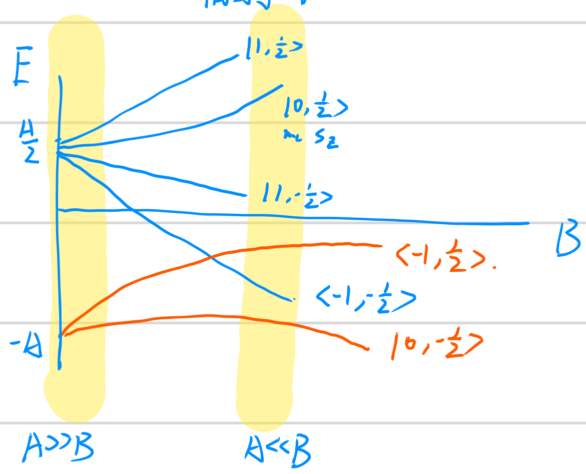


非简并微扰论:

$$E_0+E_1 = B(m_l+2S_z)\hbar + A\hbar^2 S_z m_l .$$

③ $A\sim B$ 必须整个矩阵统一对角化 (2×(2l+1)矩阵)

相当于 $\hat{V}=A\hat{\vec{L}}\cdot\hat{\vec{S}}+B(\hat{L}_z+2\hat{S}_z)$ 的简并微扰 (0级为库仑力能级).



C*. 如V对角化不能消除简并,即一级近似下能级不分裂,则必须考虑简并子空间之外的态的影响

$$|\psi\rangle = |\psi^{(0)}\rangle + |\psi^{(1)}\rangle + |\psi^{(2)}\rangle + \cdots$$

$$|\psi^{(0)}\rangle = \sum_{\mu} C^{(0)}_{m\mu}|\psi^{(0)}_{m\mu}\rangle$$

$$|\psi^{(1)}\rangle = \sum_{n\neq m} C^{(1)}_{n}|\psi^{(0)}_{n}\rangle$$

$$|\psi^{(2)}\rangle = \sum_{n\neq m} C^{(2)}_{n}|\psi^{(0)}_{n}\rangle$$ ($|\psi^{(1)}\rangle$ 也正交于简并子空间)

$$\begin{cases}(\hat{H}_0-E^{(0)}_m)|\psi^{(0)}_n\rangle = 0 & 0次\\ (\hat{H}_0-E^{(0)}_m)|\psi^{(1)}\rangle = (E^{(1)}-\hat{V})|\psi^{(0)}\rangle & 1次\\ (\hat{H}_0-E^{(0)}_m)|\psi^{(2)}\rangle = (E^{(1)}_n-\hat{V})|\psi^{(1)}\rangle + E^{(2)}_m|\psi^{(0)}\rangle & 2次\end{cases}$$

$\langle\psi^{(0)}_{m\nu}|$ 左乘λ的1次项式

$$\sum_{\mu}\left[V_{m\nu,m\mu} - \delta_{\mu,\nu}E^{(1)}_m\right]C^{(0)}_{m\mu} = 0$$

如 $V_{m\nu,m\mu}$ 对角且对角元相等,则能级在一级近似下依然简并 (对不同态作用效果相同)

$\langle\psi^{(0)}_{m\nu}|$ 左乘λ的2次项式

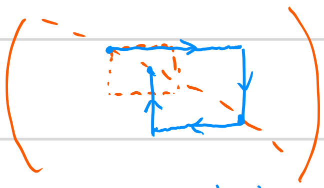
非对角元.

$$E^{(2)}_m C^{(0)}_{m\nu} = \sum_{n\neq m} V_{m\nu,n} C^{(1)}_n$$

$\langle\psi^{(0)}_n|$ 左乘λ的1次项式

$$(E_n^{(0)} - E_m^{(0)}) C_n^{(1)} = -\sum_\mu V_{n,m\mu} C_{m\mu}^{(0)}$$

可以看到当$\nu,\mu=1$时，回归非简并微扰论



简并二阶微扰
耦合到不同态上

$$\Rightarrow C_n^{(1)} = \sum_\mu \frac{V_{n,m\mu}}{E_m^{(0)} - E_n^{(0)}} C_{m\mu}^{(0)}$$

联立 $\Rightarrow$ $$\sum_\mu \underbrace{\sum_{n\neq m} \frac{V_{m\nu,n} V_{n,m\mu}}{E_m^{(0)} - E_n^{(0)}}}_{\nu,\mu\text{为自由指标}} C_{m\mu}^{(0)} = E_m^{(2)} C_{m\nu}^{(0)}$$

$\nu\mu$矩阵的本征方程，得到 $C_{m\mu}^{(0)}, E_m^{(2)}$

例： $$H = \begin{pmatrix} E_1 & & a \\ & E_1 & b \\ a^* & b^* & E_2 \end{pmatrix}$$

(i) 简并子空间 $E^{(1)} = 0$

$$\begin{pmatrix} \frac{|a|^2}{E_1-E_2} & \frac{ab^*}{E_1-E_2} \\ \frac{a^*b}{E_1-E_2} & \frac{|b|^2}{E_1-E_2} \end{pmatrix}$$

都是二阶的

的本征问题的解为 $E_1^{(2)} = 0, \frac{|a|^2+|b|^2}{E_2-E_1}$ $\Rightarrow \begin{cases} E_1 \\ E_1 + \frac{|a|^2+|b|^2}{E_2-E_1} \end{cases}$

(ii) 非简并子空间 $$E_2 + \frac{|a|^2+|b|^2}{E_2-E_1}$$

例：自旋$\frac{1}{2}$的三维各向同性谐振子，处于基态，在微扰 $\hat V = \lambda \hat\sigma_z \hat z$ 的作用下，求基态能级准确到二阶

基态空间 $\{|n_x, n_y, n_z, \uparrow\rangle, |n_x, n_y, n_z, \downarrow\rangle\}$

$$\hat z = \sqrt{\frac{\hbar}{2m\omega}} (\hat a^+ + \hat a)$$

$$\begin{array}{c|cccc} & |0,0,0,\uparrow\rangle & |0,0,0,\downarrow\rangle & |0,0,1,\uparrow\rangle & |0,0,1,\downarrow\rangle \\ \hline \langle 0,0,0,\uparrow| & 0 & 0 & \sqrt{\frac{\hbar}{2m\omega}}\lambda & 0 \\ \langle 0,0,0,\downarrow| & 0 & 0 & 0 & -\sqrt{\frac{\hbar}{2m\omega}}\lambda \\ \langle 0,0,1,\uparrow| & \sqrt{\frac{\hbar}{2m\omega}}\lambda & 0 & 0 & 0 \\ \langle 0,0,1,\downarrow| & 0 & -\sqrt{\frac{\hbar}{2m\omega}}\lambda & 0 & 0 \end{array}$$

E_0 简并微扰： $$\begin{pmatrix} -\frac{\lambda^2}{2m\omega^2} & 0 \\ 0 & -\frac{\lambda^2}{2m\omega^2} \end{pmatrix}$$

二阶修正仍简并 $$E \approx \frac{3}{2}\hbar\omega - \frac{\lambda^2}{2m\omega^2}$$

例 自旋 $\frac{1}{2}$ 的三维各向同性谐振子，处于基态，在微扰 $\hat{V}=\lambda\hat{\sigma}_x\hat{y}^2$ 的作用下，求基态能级准确到二阶

基态空间 $\{|n_x,n_y,n_z,\uparrow\rangle,\ |n_x,n_y,n_z,\downarrow\rangle\}$

$$\hat{y}^2=\frac{\hbar}{2m\omega}(\hat{a}^2+\hat{a}^{\dagger 2}+2\hat{a}^\dagger\hat{a}+1)$$

$$\begin{array}{c|cccc} & |0,0,0,\uparrow\rangle & |0,0,0,\downarrow\rangle & |0,2,0,\uparrow\rangle & |0,2,0,\downarrow\rangle \\ \hline \langle 0,0,0,\uparrow| & \frac{3}{2}\hbar\omega & \frac{\hbar}{2m\omega}\lambda & 0 & \frac{\sqrt{2}\hbar}{2m\omega}\lambda \\ \langle 0,0,0,\downarrow| & \frac{\hbar}{2m\omega}\lambda & \frac{3}{2}\hbar\omega & \frac{\sqrt{2}\hbar}{2m\omega}\lambda & 0 \\ \langle 0,2,0,\uparrow| & 0 & \frac{\sqrt{2}\hbar}{2m\omega}\lambda & \frac{7}{2}\hbar\omega & \frac{\hbar}{2m\omega}\lambda \\ \langle 0,2,0,\downarrow| & \frac{\sqrt{2}\hbar}{2m\omega}\lambda & 0 & \frac{\hbar}{2m\omega}\lambda & \frac{7}{2}\hbar\omega \end{array}$$

一阶：$\frac{3}{2}\hbar\omega\pm\frac{\hbar}{2m\omega}\lambda$

二阶：对 $\frac{3}{2}\hbar\omega-\frac{\hbar}{2m\omega}\lambda$ ：$|\psi^{(0)}\rangle=\frac{\sqrt{2}}{2}(|0,0,0,\uparrow\rangle-|0,0,0,\downarrow\rangle)$、

$$E^{(2)}=\frac{|\langle 0,2,0,\uparrow|\hat{V}|\psi^{(0)}\rangle|^2+|\langle 0,2,0,\downarrow|\hat{V}|\psi^{(0)}\rangle|^2}{\frac{3}{2}\hbar\omega-\frac{7}{2}\hbar\omega}=-\frac{\hbar\lambda^2}{4m^2\omega^3}$$

$$-\frac{\left|-\frac{\sqrt{2}\hbar}{2m\omega}\lambda\right|^2+\left|\frac{\sqrt{2}\hbar}{2m\omega}\lambda\right|^2}{4\hbar\omega}$$

对 $\frac{3}{2}\hbar\omega+\frac{\hbar}{2m\omega}\lambda$ ：$|\psi^{(0)}\rangle=\frac{\sqrt{2}}{2}(|0,0,0,\uparrow\rangle+|0,0,0,\downarrow\rangle)$.

$$E^{(2)}=-\frac{\hbar\lambda^2}{4m^2\omega^3}$$

d. 微扰论在氢原子中的应用.

零级近似：$H_0=-\frac{\hbar^2}{2m}\nabla^2+V(r)$ Coulomb $\Rightarrow |n,l,m\rangle$ $E_n=-\left(\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right)\frac{1}{n^2}$ $2n^2$重简并

① 精细结构

i) 相对论修正 $T=\frac{p^2}{2m}\Rightarrow T=\sqrt{p^2c^2+m^2c^4}-mc^2\approx\frac{p^2}{2m}-\frac{p^4}{8m^3c^2}$

量子化 $[\hat{p}^4,\hat{L}^2]=[\hat{p}^2,\hat{L}_z]=0$

$\{\hat{L}^2,\hat{L}_z\}$ $E_r=\langle n,l,m|\frac{-\hat{p}^4}{8m^3c^2}|n,l,m\rangle=-\frac{E_n^2}{2mc^2}\left(\frac{4n}{l+\frac{1}{2}}-3\right)$ $\frac{E_n}{mc^2}\sim10^{-5}$

(ii) 自旋-轨道耦合

$$\hat{H}_{so}=\frac{e^2}{8\pi\varepsilon_0}\frac{1}{m^2}\frac{1}{c^2r^3}\hat{L}\cdot\hat{S}$$

$[\hat{H}_{so},\hat{L}^2]=[\hat{H}_{so},\hat{S}^2]=0$ 但 $[\hat{H}_{so},\hat{L}_z]\neq0$ $[\hat{H}_{so},\hat{S}_z]\neq0$

$[\hat{H}_{so},\hat{J}^2]=0$ $[\hat{H}_{so},\hat{J}_z]=0$ $\Rightarrow$ 选择耦合表象

$\{|n,l,s,j,m_j\rangle\}$

$$E_{so}=\frac{E_n^2}{mc^2}\left\{\frac{n[j(j+1)-l(l+1)-\frac{3}{4}]}{l(l+\frac{1}{2})(l+1)}\right\}$$

精细结构总影响

$$E_{n,j} = E_n + \frac{E_n^2}{2mc^2}\left(3 - \frac{4n}{j+\frac{1}{2}}\right) = \frac{E_0}{n^2}\left[1+\frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right]$$

② Zee Man Effect

③ 超精细结构

核自旋与电子轨道/自旋的相互作用 $\hat{H}_{hf} \sim \vec{I}\cdot\vec{J}$

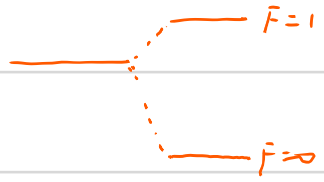
$l=0$: 定义 $\vec{F} = \vec{I} + \vec{L} + \vec{S}$ $\quad [\hat{F}^2, \hat{H}_{hf}] = [\hat{F}_z, \hat{H}_{hf}] = 0$

$\{|n, l, s, j, I, F, m_f\rangle\}$ $\quad l=0,\ s=\frac{1}{2},\ I=\frac{1}{2}$, $\Rightarrow J=\frac{1}{2}$ $\Big\}\Rightarrow F=0,1$

$$E_{hf}^{(1)} = \langle n,l,j,s,I,F,m_F | \hat{H}_{hf} | n,l,j,s,I,F,m_F\rangle$$

$$= \frac{1}{2}A\left[F(F+1) - I(I+1) - s(s+1)\right]\hbar^2$$

$$= A\hbar^2 \begin{cases} \frac{1}{4} & \text{三重态} \\ -\frac{3}{4} & \text{单态} \end{cases}$$



2.变分法

对于给定 $\hat{H}$,和任意态 $|\psi\rangle$,均有如下关系.

$$\langle\psi|\hat{H}|\psi\rangle \geq E_{gs} \text{ 基态能量}$$

$$\langle\psi|\hat{H}|\psi\rangle = \sum_n |C_n|^2 E_n$$

PS: 用 $\hat{P} = \hat{I} - |\psi_{min}\rangle\langle\psi_{min}|$.

$\hat{H}' = \hat{P}\hat{H}\hat{P}$ 可用变分法求第一激发态

应用: 猜基态的形式,变成最优化问题

$|\psi(a_n)\rangle$, 其中 $\{a_n\}$ 为参数

$$E(a_n) = \frac{\langle\psi(a_n)|\hat{H}|\psi(a_n)\rangle}{\langle\psi(a_n)|\psi(a_n)\rangle}$$

求 $\{a_n\}$ 使 $E(a_n)$ 取极小值 $\frac{\partial E(a_n)}{\partial a_n} = 0 \Rightarrow E_{gs}$ 近似值.

关键: 怎么猜 $\{|\psi(a_n)\rangle\}$ 使得子空间离 GS 足够近? (成功理论总是做到的).

例: He 原子 (Griffith)

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{2}{r_1}+\frac{2}{r_2}-\frac{1}{|\vec{r}_1-\vec{r}_2|}\right) = \underbrace{-\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2) - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{Z}{r_1}+\frac{Z}{r_2}\right)}_{H_0} + \frac{e^2}{4\pi\varepsilon_0}\left(\underbrace{\frac{Z-2}{r_1}+\frac{Z-2}{r_2}}_{H_1} + \underbrace{\frac{1}{|\vec{r}_1-\vec{r}_2|}}_{V}\right).$$

由 H 原子波函数 $\langle\vec{r}|n,l,m\rangle = \frac{1}{\sqrt{\pi a^3}} e^{-\frac{r}{a}}$ 启发

设 $\psi(\vec{r}_1, \vec{r}_2) = \frac{Z^3}{\pi a^3} e^{-\frac{Z(r_1+r_2)}{a}}$ $\quad$ (期待 $Z<2$).

$$\langle H_0\rangle = 2Z^2 E_1$$

$$\langle H_1\rangle = 2(Z-2)\frac{e^2}{4\pi\varepsilon_0}\underbrace{\left\langle\frac{1}{r}\right\rangle}_{\frac{Z}{a}} \Rightarrow \langle H\rangle = \left[-2Z^2 + \frac{27}{4}Z\right]E_1 \quad \frac{d\langle H\rangle}{dZ} = 0 \Rightarrow Z \approx \frac{27}{16} \quad \langle H\rangle = \frac{27^2}{16\times 8}E_1 \simeq -77.5\ \text{eV}$$

$$\langle V\rangle = -\frac{5}{4}ZE_1$$

(实验上为 -78.795 eV)

3、含时微扰

a 基本理论（迭代形式）

跃迁的解释 $|\psi_n\rangle \to |\psi_m\rangle$ $\quad \hat{H}_0|\psi_n\rangle = E_n|\psi_n\rangle$

$$\hat{H} = \hat{H}_0 + \underbrace{\hat{V}(t)}_{\text{含时微扰项}}$$

设 $|\psi\rangle = \sum_n C_n(t)|\psi_n\rangle$，代入 $i\hbar\frac{\partial}{\partial t}|\psi\rangle = (\hat{H}_0 + \hat{V})|\psi\rangle$

$\Rightarrow i\hbar\frac{\partial}{\partial t}C_m(t) = E_m C_m(t) + \sum_n V_{mn}(t)C_n(t)$. 矩阵形式：$i\hbar\frac{\partial}{\partial t}\begin{pmatrix} C_m \end{pmatrix} = \begin{pmatrix} E_1 & & \\ & \ddots & \\ & & E_n \end{pmatrix}\begin{pmatrix} C_m \end{pmatrix} + \begin{pmatrix} & V_{mn} & \end{pmatrix}\begin{pmatrix} C_m \end{pmatrix}$.

作变换 $\tilde{C}_n(t) = e^{i\frac{E_n t}{\hbar}} C_n(t)$ $\Rightarrow i\hbar\frac{\partial}{\partial t}\tilde{C}_n(t) = -E_n\tilde{C}_n(t) + e^{i\frac{E_n t}{\hbar}} i\hbar\frac{\partial}{\partial t}C_n(t)$.

$\Rightarrow i\hbar\frac{\partial}{\partial t}\tilde{C}_m(t) = \sum_n V_{mn}(t)\, e^{i\frac{(E_m-E_n)t}{\hbar}}\,\tilde{C}_n(t)$ 定义 $\omega_{mn} = (E_m - E_n)/\hbar$

$\Rightarrow i\hbar\frac{\partial}{\partial t}\tilde{C}_m(t) = \sum_n V_{mn}(t)\, e^{i\omega_{mn}t}\,\tilde{C}_n(t)$ （相互作用绘景）

将本征能量放在相位里

有 V_{mn} 说明是升一阶

rotating frame

迭代微扰：

i) $t=0$ 时的初态为零级近似

ii) 零级近似代入上式右边 $\Rightarrow$ 一级修正

iii) 反复迭代求更高阶修正

例：二能级系统 $V(t)$ $|b\rangle$ $|a\rangle$

$$i\hbar\frac{\partial}{\partial t}\tilde{C}_a = V_{aa}\tilde{C}_a + V_{ab}e^{i\omega_{ab}t}\tilde{C}_b$$
$$i\hbar\frac{\partial}{\partial t}\tilde{C}_b = V_{bb}\tilde{C}_b + V_{ba}e^{i\omega_{ba}t}\tilde{C}_a$$
$$\Leftarrow\quad i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\tilde{C}_a\\ \tilde{C}_b\end{pmatrix} = \begin{pmatrix} V_{aa} & V_{ab}e^{i\omega_{ab}t} \\ V_{ba}e^{i\omega_{ba}t} & V_{bb}\end{pmatrix}\begin{pmatrix}\tilde{C}_a\\ \tilde{C}_b\end{pmatrix}.$$

设 $\tilde{C}_a(0)=1$ $\quad \tilde{C}_b(0)=0$ 零级 $\quad (C_a(0) = e^{-i\frac{E_a}{\hbar}t}$ $\quad C_b(0)=0)$

一级修正

$$\begin{cases} i\hbar\frac{\partial}{\partial t}\tilde{C}_a^{(1)} = V_{aa} \\ i\hbar\frac{\partial}{\partial t}\tilde{C}_b^{(1)} = V_{ba}e^{i\omega_{ba}t}\end{cases} \Rightarrow \begin{cases}\tilde{C}_a^{(1)} = -\frac{i}{\hbar}\int_0^t V_{aa}(t')dt' \\ \tilde{C}_b^{(1)} = -\frac{i}{\hbar}\int_0^t V_{ba}(t')e^{i\omega_{ba}t'}dt'\end{cases}$$

二级修正：

$$i\hbar\frac{\partial}{\partial t}\tilde{C}_a^{(2)} = V_{aa}\tilde{C}_a^{(1)} + V_{ab}e^{i\omega_{ab}t}\tilde{C}_b^{(1)}$$

$$\Rightarrow \tilde{C}_a^{(2)} = \cdots\cdots$$

$\Rightarrow$ 准确到一级修正：

$$\begin{cases}\tilde{C}_a(t) = \overset{0\text{级}}{1} - \underbrace{\left(\frac{i}{\hbar}\right)\int_0^t V_{aa}(t')dt'}_{1\text{级}} + o(V^2) \\ \tilde{C}_b(t) = -\left(\frac{i}{\hbar}\right)\int_0^t V_{ba}(t')e^{i\omega_{ba}t'}dt' + o(V^2)\end{cases}$$

$$|\tilde{C}_a|^2 + |\tilde{C}_b|^2 = 1 + o(V^2)$$

也可以设 $\begin{cases} d_a = e^{\frac{i}{\hbar}\int_0^t V_{aa}(t')dt'}\tilde{C}_a \\ d_b = e^{\frac{i}{\hbar}\int_0^t V_{bb}(t')dt'}\tilde{C}_b \end{cases}$ $\longrightarrow$ 无简形式 ✓

b. 跃迁

$i\hbar\frac{\partial}{\partial t}\tilde{C}_m = \sum_n V_{mn}\tilde{C}_n e^{i\omega_{mn}t}$

设初态为k态 $\tilde{C}_n = \delta_{nk}$

一级含时微扰为 $i\hbar\frac{\partial}{\partial t}\tilde{C}_m^{(1)} = V_{mk}e^{i\omega_{mk}t} \Rightarrow \tilde{C}_m^{(1)} = -\frac{i}{\hbar}\int_0^t V_{mk}(t')e^{i\omega_{mk}t'}dt'$

$\Rightarrow \tilde{C}_m = \delta_{mk} - \frac{i}{\hbar}\int_0^t V_{mk}(t')e^{i\omega_{mk}t'}dt'$

对于 $m\neq k$，跃迁概率

$$P_{k\to m}(t) = \frac{1}{\hbar^2}\left|\int_0^t V_{mk}(t')e^{i\omega_{mk}t'}dt'\right|^2 \quad (m\neq k)$$

例：光场与二能级原子的耦合 $E_b - E_a = \hbar\omega_0$ ($\hbar\omega_0$: $|b\rangle \to |a\rangle$)

$V(t) = V(\vec{r})(e^{i\omega t} + e^{-i\omega t})$

i) $\langle a|V(\vec{r})|b\rangle = V_{ab}$ $\quad V_{aa} = V_{bb} = 0$. 初态为 $|a\rangle$

$$\tilde{C}_b(t) = -\frac{i}{\hbar}\int_0^t V_{ba}(e^{i\omega t'} + e^{-i\omega t'})e^{i\omega_0 t'}dt' = -\frac{V_{ba}}{\hbar}\left[\frac{e^{i(\omega_0+\omega)t}-1}{\omega_0+\omega} + \frac{e^{i(\omega_0-\omega)t}-1}{\omega_0-\omega}\right]$$

跃迁几率： $P_{a\to b}(t) = |\tilde{C}_b|^2$

rotating-wave approximate (RWA)：(将快速振荡近似掉)

当 $\omega_0 \sim \omega$ 且 $V_{ab} \ll \hbar\omega_0, \hbar\omega$ 时，$\frac{e^{i(\omega_0+\omega)t}-1}{\omega_0+\omega}$ 可忽略

$$\tilde{C}_b(t) \approx -\frac{V_{ba}}{\hbar}\frac{e^{i(\omega_0-\omega)t}-1}{\omega_0-\omega} = -\frac{V_{ba}}{\hbar}e^{i(\omega_0-\omega)\frac{t}{2}}\frac{1}{\omega_0-\omega}2i\sin\left[\frac{\omega_0-\omega}{2}t\right]$$

$\Rightarrow P_{a\to b}(t) = \frac{4|V_{ab}|^2}{\hbar^2}\frac{\sin^2\left[\frac{(\omega_0-\omega)t}{2}\right]}{(\omega_0-\omega)^2}$ 由 $\lim_{t\to\infty}\frac{\sin^2\left[(\omega_0-\omega)\frac{t}{2}\right]}{(\omega_0-\omega)^2} = \frac{\pi}{4}t\,\delta\left(\frac{\omega_0-\omega}{2}\right)$ $\quad \left(\lim_{\alpha\to\infty}\frac{\sin^2\alpha x}{\alpha x^2} = \pi\delta(x)\right)$

$P_{a\to b}(t) \xlongequal{t\to\infty} \frac{2\pi}{\hbar^2}t|V_{ba}|^2\delta(\omega_0-\omega)$ 作图

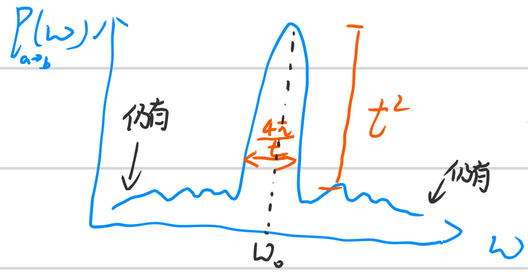
单位时间跃迁速率： $w_{a\to b} = \frac{2\pi}{\hbar^2}|V_{ab}|^2\delta(\omega_0-\omega)$

如 $|b\rangle$ 附近有很多态

态密度

$$\sum_b P_{a\to b}(t)\big|_{t\to\infty} = \int dE\,\rho(E)\frac{2\pi}{\hbar}|V_{ab}|^2\delta(E-E_b)t$$

$$\bar{w} = \rho(E_b)\frac{2\pi}{\hbar}|V_{ab}|^2$$



$\frac{4\pi\hbar}{t}$ $\nearrow$ $\delta E\,\delta t \sim \hbar$

t很小时，能量可以不守恒(微扰)

PS：上面讨论 t 不能太大： $t \ll \frac{1}{|V_{ab}|}, \frac{1}{|\omega_0-\omega|}$ (近共振解释)

ii) 严格解 (Rabi) under RWA

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}C_a\\C_b\end{pmatrix} = \begin{pmatrix}E_a & V_{ab}(e^{i\omega t}+e^{-i\omega t})\\ V_{ba}(e^{i\omega t}+e^{-i\omega t}) & E_b\end{pmatrix}\begin{pmatrix}C_a\\C_b\end{pmatrix}$$

rotating frame: $\begin{cases} \tilde{C}_a = C_a e^{i\left(\frac{E_a+E_b}{2\hbar}-\frac{\omega}{2}\right)t} \\ \tilde{C}_b = C_b e^{i\left(\frac{E_a+E_b}{2\hbar}+\frac{\omega}{2}\right)t} \end{cases}$ $\Rightarrow i\frac{\partial}{\partial t}\begin{pmatrix}\tilde{C}_a\\ \tilde{C}_b\end{pmatrix} = \begin{pmatrix} \frac{\delta}{2} & \frac{V_{ab}}{\hbar}(1+e^{-i2\omega t}) \\ \frac{V_{ba}}{\hbar}(1+e^{i2\omega t}) & -\frac{\delta}{2}\end{pmatrix}\begin{pmatrix}\tilde{C}_a\\ \tilde{C}_b\end{pmatrix}$

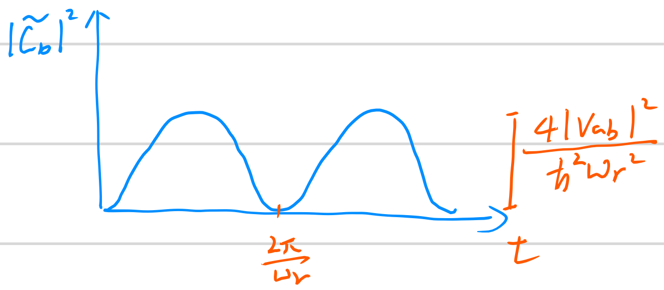
(其中 $\delta = \omega-\omega_0$)　失谐 $\begin{cases}\delta<0 & 红\\ \delta>0 & 蓝\end{cases}$

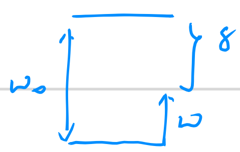
RWA: $i\frac{\partial}{\partial t}\begin{pmatrix}\tilde{C}_a\\ \tilde{C}_b\end{pmatrix} = \begin{pmatrix}\frac{\delta}{2} & \frac{V_{ab}}{\hbar}\\ \frac{V_{ba}}{\hbar} & -\frac{\delta}{2}\end{pmatrix}\begin{pmatrix}\tilde{C}_a\\ \tilde{C}_b\end{pmatrix}$ (不含时) $\Rightarrow \begin{cases}\tilde{V} = \frac{\delta}{2}\sigma_z + \mathrm{Re}\left(\frac{V_{ab}}{\hbar}\right)\sigma_x - \mathrm{Im}\left(\frac{V_{ab}}{\hbar}\right)\sigma_y \\ \begin{pmatrix}\tilde{C}_a(t)\\ \tilde{C}_b(t)\end{pmatrix} = e^{-i\tilde{V}t}\begin{pmatrix}\tilde{C}_a(0)\\ \tilde{C}_b(0)\end{pmatrix}\end{cases}$

由 $e^{-i\varphi\vec{\sigma}\cdot\vec{n}} = \cos\varphi\,\hat{I} - i\sin\varphi(\vec{\sigma}\cdot\vec{n})$

$$\Rightarrow \begin{pmatrix}\tilde{C}_a(t)\\ \tilde{C}_b(t)\end{pmatrix} = \begin{pmatrix}\cos\frac{\omega_r}{2}t + i\frac{\delta}{\omega_r}\sin\frac{\omega_r}{2}t & -i\frac{2V_{ab}}{\hbar\omega_r}\sin\frac{\omega_r t}{2} \\ -i\frac{2V_{ab}^*}{\hbar\omega_r}\sin\frac{\omega_r t}{2} & \cos\frac{\omega_r}{2}t - i\frac{\delta}{\omega_r}\sin\frac{\omega_r}{2}t\end{pmatrix}\begin{pmatrix}\tilde{C}_a(0)\\ \tilde{C}_b(0)\end{pmatrix}.$$

$\left(\omega_r = \sqrt{\delta^2+\frac{4|V_{ab}|^2}{\hbar^2}}\right)$　如 $\begin{cases}\tilde{C}_a(0)=1\\ \tilde{C}_b(0)=0\end{cases} \Rightarrow \tilde{C}_a(t) = \cos\frac{\omega_r}{2}t + i\frac{\delta}{\omega_r}\sin\frac{\omega_r}{2}t. \longrightarrow$ Rabi 振荡　最早 $t=\frac{2\pi}{\omega_r}$ 时 $|\tilde{C}_a(t)|^2=1.$

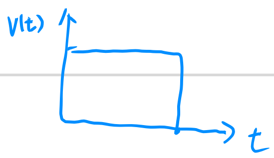




$|\delta| \gg |V_{ab}| \longrightarrow$ 两能级近似很正确，之上的能级离共振态太远，不会有太多占据

c. 含时问题的特例

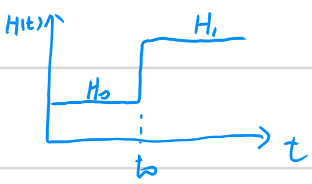
① 常微扰



初态 $|n\rangle$，末态 $|m\rangle$

一阶修正：$\tilde{C}_m^{(1)}(t) = -\frac{i}{\hbar}\int_0^t V_{mn}e^{i\omega_{mn}t'}dt'$　✓.

② 突变近似

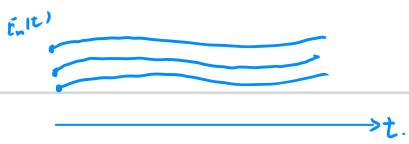


在 t_0 时刻 $\hat{H}$ 突变，态近似不变　$\hat{H}_0|\psi_n\rangle = E_n|\psi_n\rangle$　$\hat{H}_1|\psi_\alpha\rangle = E_\alpha|\psi_\alpha\rangle$

$0<t<t_0$: $|\psi\rangle = \sum_n C_n e^{-i\frac{E_n t}{\hbar}}|\psi_n\rangle$　　$t>t_0$: $|\psi\rangle = \sum_n C_n e^{-i\frac{E_n t_0}{\hbar}}\sum_\alpha\langle\psi_\alpha|\psi_n\rangle|\psi_\alpha\rangle e^{-iE_\alpha(t-t_0)/\hbar}$

③ 绝热近似

$H(t)$ 缓变，则初始本征态绝热跟随当前 $H(t)$ 的本征态演化



$t>0$: $|\psi(t)\rangle \approx \underbrace{e^{i\theta_n(t)}}_{\text{动力学相位}}\underbrace{e^{i\gamma_n(t)}}_{\text{几何相位}}|\psi_n(t)\rangle$

$\theta_n = -\frac{1}{\hbar}\int_0^t E_n(t')dt'$

$\gamma_n = i\int_0^t\langle\psi_n(t')|\frac{\partial}{\partial t'}|\psi_n(t')\rangle dt'$

绝热条件：$\Delta E \gg \frac{\hbar}{t}$